

AD-A251 985



REPORT DOCUMENTATION PAGE

Form Approved
GSA No. 0704-0188

Use in estimates to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and reviewing the collection of information, and comments regarding this burden estimate or any other aspect of this burdening this burden. To Washington Headquarters Service, Directorate for Information Operations and Reports, 1215 Jefferson Ave., Washington, DC 20540-6001, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

2. REPORT DATE
05-15-923. REPORT TYPE AND DATES COVERED
Technical 06-01-91 to 05-31-92

4. TITLE AND SUBTITLE

3-d Periodic Packaging: Sodalite, A Model System

5. FUNDING NUMBERS

N00014-81-K-0598

6. AUTHOR(S)

G.D. Stucky, V.I. Srdanov, W.T.A. Harrison, T.E. Gier,
N.L. Keder, K.L. Moran, K. Haug, and H.I. Metiu

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of California
Department of Chemistry
Santa Barbara, CA 93106DTIC
ELECTE
JUN 25 1992
S B D8. PERFORMING ORGANIZATION
REPORT NUMBER

T10

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
Chemistry Program
800 N. Quincy Street
Alexandria, VA 2221710. SPONSORING/MONITORING
AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Prepared for Publication in Supramolecular Chemistry, American Chemical Society
Symposium Series

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release;
distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The 3-d periodicity of molecular sieve surfaces coupled with the ability to vary pore size, topology and chemical potential of the framework permits considerable latitude in the assembly of confined atomic and molecular arrays. Sodalite, one of the simplest zeolite analogue structures with a 60 atom cage can be synthesized with a broad range of different atoms to give effective cage charges varying from 0 to -6. Non-hydrogen atom clusters of up to 9 atoms and hydrogen atom containing clusters with as many as 17 atoms can be assembled within the cage during synthesis or by gas phase or ion exchange inclusion. The optical and structural properties of the included clusters can be systematically modified by changes in the cage dimensions and framework electric field. The structure of both the frameworks and the clusters within the cages of sodalite structural analogues can be precisely determined. In addition to new framework compositions with the sodalite structure, approaches to synthesize new classes of materials consisting of semiconductor, metal or molecular clusters confined within open framework structures are discussed.

14. SUBJECT TERMS

15. NUMBER OF PAGES

16

16. PRICE CODE

17. SECURITY CLASSIFICATION
OF REPORT
Unclassified18. SECURITY CLASSIFICATION
OF THIS PAGE
Unclassified19. SECURITY CLASSIFICATION
OF ABSTRACT
Unclassified20. LIMITATION OF ABSTRACT
UL

OFFICE OF NAVAL RESEARCH

Contract N00014-81-K-0598

R&T Code N47092

Technical Report No. 10

**3-d Periodic Packaging:
Sodalite, a Model System**

by

**G.D. Stucky, V.I. Srdanov, W.T.A. Harrison, T.E. Gier,
N.L. Keder, K.L. Moran, K. Haug, and H.I. Metiu**

Prepared for Publication in

***Supramolecular Chemistry*, American Chemical
Society Symposium Series**

May 15, 1992

Reproduction in whole or in part is permitted for any purpose of the United State Government.

This document has been approved for public release and sale; its distribution is unlimited.

This statement should also appear in Item 12 of the Report Documentation Page, Standard Form 298. Your contract number and R&T Code should be reported in Item 5 of Standard Form 298. Copies of the form are available from your cognizant grant or contract administrator.



3-d Periodic Packaging: Sodalite, A Model System

G. D. Stucky, V. I. Srdanov, W. T. A. Harrison, T. E. Gier,
N. L. Keder, K. L. Moran, K. Haug, and H. I. Metiu

Department of Chemistry, University of California
Santa Barbara, California, 93106-9510

The 3-d periodicity of molecular sieve surfaces coupled with the ability to vary pore size, topology and chemical potential of the framework permits considerable latitude in the assembly of confined atomic and molecular arrays. Sodalite, one of the simplest zeolite analogue structures with a 60 atom cage can be synthesized with a broad range of different atoms to give effective cage charges varying from 0 to -6. Non-hydrogen atom clusters of up to 9 atoms and hydrogen atom containing clusters with as many as 17 atoms can be assembled within the cage during synthesis or by gas phase or ion exchange inclusion. The optical and structural properties of the included clusters can be systematically modified by changes in the cage dimensions and framework electric field. The structure of both the frameworks and the clusters within the cages of sodalite structural analogues can be precisely determined. In addition to new framework compositions with the sodalite structure, approaches to synthesize new classes of materials consisting of semiconductor, metal or molecular clusters confined within open framework structures are discussed.



Recent progress towards the goal of nanostructure photonic and electronic components has evolved into the development of commercial devices which are currently in the range of 0.5 to 1 μm in size. 1-d confinement of atomic or molecular monolayers ($\sim 5 \text{ \AA}$) by molecular beam epitaxy (MBE), electrochemical, atomic layer epitaxy (ALE) and Langmuir Blodgett approaches has been well documented. However, generation of 2-d and 3-d confined structures by using tilted superlattices or related approaches has so far given only mixed results,

For	
<input checked="checked" type="checkbox"/>	
<input type="checkbox"/>	
<input type="checkbox"/>	
ion	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

primarily because of lateral resolution limitations ($\sim 100\text{\AA}$). Another dimension of sophistication is required to precisely fabricate periodic 3-d structures with confinement sizes below 100\AA . In this size regime, where the volume to surface area ratio of the bulk material rapidly decreases, one finds the transition from extended band structure to quantum confined structure, i.e. the interface between solid state and molecular inorganic chemistry. This fascinating area of cluster chemistry is currently being intensively investigated by synthetic chemists, theorists and device engineers.

There are several important requirements related to the properties of an ideal 3-d heterostructure. These include:

- size and topographical uniformity
- 3-d periodicity
- tunability with respect to atomic modification of
 - topography
 - cluster dimensions
 - surface states defined by the cluster/packaging interface
 - intercluster coupling
- thermal and optical stability of both substrate and the 3-d clusters
- optical transparency of the 3-d enclosure surface

Currently, there are few examples of structurally defined 3-d periodic arrays of packaged clusters. As a packaging medium, molecular sieves have the potential to be used to generate 3-d heterostructures consisting of ordered assemblies of various clusters with sizes between $6\text{-}13\text{\AA}$. In this family, the sodalite structure has the simplest cage and 3-d periodic geometry with exceptional crystallinity. As such, it provides an excellent opportunity to investigate how one might use host composition to control cluster structure and electronic properties.

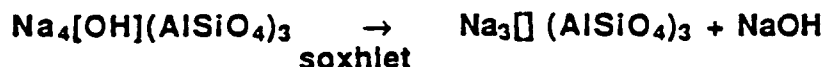
An Inorganic 60 Atom Cage

Figure 1 shows the truncated octahedron of the sodalite structure and for comparison the truncated icosahedron found for C_{60} buckminsterfullerene(1). The truncated octahedron is constructed with tetrahedrally coordinated metal atoms (Si,Al) which are linked by corner sharing oxygen atoms. The upper right hand part of Figure 1 shows only the 24 metal atoms which make up the sodalite cage. The 36 connecting oxygen atoms (lower part of Figure 1) make up the remainder of the 60 atoms in the polyhedron. A hypothetical organic analog would be a saturated polyether. The pore openings are typically described as "6 rings" (metal atoms only) which are in fact 12 atom ring openings with alternating metal and oxygen atoms, while the "4 rings" correspondingly define 8 atom ring openings. In the remainder of this paper we will retain the usual zeolite molecular sieve convention of denoting these pores by the metal atoms only (i.e. as 6 rings and 4 rings). This simple cage structure is an important fundamental building block in molecular sieve and zeolite chemistry and can be used to generate

open zeolite structures by structural architecture based on putting together "clusters of cages" as in zeolite A, zeolite X or Y, and the hexagonal form of zeolite Y.

There are a large number of atomic and molecular clusters that can be synthesized within the sodalite cage. An example is the eight atom cubane-like cluster formed by cadmium sulfide in the sodalite (β) cages of zeolite Y (Figure 2) (2). Na_4ClO_3 is an 8 atom cluster found in the sodalite cage with a different geometry, i.e. a cubane type structure with one oxygen atom missing from a corner site and a chlorine atom at the center.(3) The five atom M_4X cluster (Figure 3) is illustrated for Zn_4S in $\text{Zn}_4\text{S}(\text{BeSiO}_4)_3$ (4) and discussed in more detail below. One can have at least 9 non-hydrogen atoms, or as many as 17 atoms if hydrogen atoms are included, within a sodalite cage (Table 1).

The term "empty cage" is used to refer to structures which do not contain atoms at the center of the cage. This is denoted in empirical formulae by \square , e.g. $\text{Na}_3\square(\text{AlSiO}_4)_3$ for an "empty" cage containing $[\text{Na}_3]^{3+}$, versus $\text{Na}_4\text{Br}(\text{AlSiO}_4)_3$ for a "filled" cage containing $[\text{Na}_4\text{Br}]^{3+}$. The sodium atoms of the $[\text{Na}_4\text{Br}]^{3+}$ cluster are tetrahedrally located at four of the 6 ring windows as illustrated for $[\text{Zn}_4\text{S}]^{6+}$ in Figure 3. Removal of the Br⁻ atom from the center of the cage and one sodium atom from the $[\text{Na}_4]^{3+}$ tetrahedron along with some displacement of the sodium atoms gives the topography of the $[\text{Na}_3]^{3+}$ cluster. Empty cage structures can be made by direct synthesis or by the reactions indicated below (i.e. starting with a sodalite which has a hydroxide group at the center of the cage) in which sodium hydroxide is removed by extraction to give "empty cages" containing three sodium atoms(5).



Alternatively, a specified number of empty and filled cages can be synthesized by starting with a material which has some cages containing hydroxide and others containing the desired atoms. Hydroxide extraction then will leave the desired fraction of cages filled with the cluster surrounded by empty cages.

Numerous other cage geometries and charges are accessible such as the 4-9 combination, $\text{Na}_8[\text{SO}_4]\square(\text{AlSiO}_4)_6$ (6) (an equal number of cages containing four atom $[\text{Na}_4]^{4+}$ and nine atom $[\text{Na}_4\text{SO}_4]^{2+}$ clusters), the 5 atom mixed cluster found in $[\text{Zn}_3\text{GaAs}](\text{BO}_2)_{12}$ (7) and clusters designed for ternary metal atom cages as in $[(\text{CH}_3)_4\text{N}](\text{MgAl}_2\text{P}_3\text{O}_{12})$ (8).

The sodalite crystal structure is usually a cubic close packed array of truncated octahedral cages, however, lower crystallographic symmetries including tetragonal, hexagonal, and orthorhombic can be obtained by appropriate framework atom substitutions. Using different atomic group compositions also modifies the cage size, cage electric field and dielectric properties. Examples of sodalites are known with all of

the group combinations shown in Table 2. Note that the formal sodalite cage charge varies from 0 to -6.

The cages can be considered as potential wells with barriers between the cages dependent upon framework dielectric properties (i.e. framework charge and atomic composition). In the following discussion, we will consider how the cage electric field, the cage geometry and the intercage separation influence cluster properties.

Optical Spectra and the Cage Electric Field

One of the simplest, but most intriguing clusters is synthesized by gas phase deposition and consequent diffusion of sodium atoms into an "empty" cage $[\text{Na}_3]^{3+}$ to give a four sodium atom cluster, $[\text{Na}_4]^{3+}$, with an unpaired delocalized electron within the cage (9),(10),(11),(12). The UV-VIS absorption spectrum of the Na_4^{3+} -sodalite is dominated by an electronic transition between the internal Stark effect broadened ground and first excited state of the Na_4^{3+} cluster. EPR studies of this sodalite "electride" have been discussed previously (10,11,12); however, no quantitative measurements have been previously reported for the optical properties of this phase.

In a recent experiment(13) the sodium vapor emerging from a temperature controllable source inside a high vacuum apparatus for metal vapor deposition(14) was deposited onto the surface of the $\text{Na}_3\text{[AlSiO}_4\text{]}_3$ sodalite at a background pressure of $P=1 \times 10^{-7}$ torr. A series of samples was prepared with different concentrations of $[\text{Na}_4]^{3+}$ clusters formed by diffusion of sodium atoms into the "empty" $\text{Na}_3\text{[AlSiO}_4\text{]}_3$ sodalite cages. The diffuse reflectance spectra of the samples containing approximately one $[\text{Na}_4]^{3+}$ cluster per 50, 10 and 4 empty cages are shown in Figure 4.

The spectrum corresponding to the lowest concentration ratio (1:50) is shown on an expanded scale in Figure 6. This defines the absorption spectrum of an isolated Na_4^{3+} color center. An additional band appears in the UV region of the spectrum ($\sim 38,000 \text{ cm}^{-1}$) as soon as the increasing concentration of sodium atoms leads to the formation of Na_4^{3+} clusters in adjacent cages. This band expands into the IR region as more of the 14 nearest neighbor (eight via 6-rings and 4 via 4-rings) cages are filled around a given Na_4^{3+} cluster cage, leading at the end to a black metallic(9) material.

Time dependent first order perturbation theory calculations to determine the absorption cross section for the Na_4^{3+} clusters in $\text{Na}_{3+x}\text{[e]}_x\text{[AlSiO}_4\text{]}_3$ can be carried out rigorously for this one electron problem(15) using the cage potential field and the cluster geometry as input parameters. The hypothetical four atom Na_4^{3+} cluster in free space would show a single absorption line at 3.2 eV. This line is split into a multiplet by the sodalite cage electric field and by higher energy transitions to the framework states.

Several semiempirical calculations (16),(17),(18),(19). have been carried out to determine the cage and framework potential of aluminosilicates, with widely varying results for the implied framework atom charges. The optical properties are clearly a sensitive function of

charge as shown in Figure 5 for theoretical results obtained using recently published cage electric field parameters(20),(21),(22),(23) with a fixed polarization direction and zeolite orientation. The spectrum is also sensitive to Na-Na distances, which are presently being characterized. The best agreement between theory and experiment is shown in Figure 6. The theoretical model is for the orientationally averaged, high resolution spectrum with the following framework charges: Si=+1.5, Al=0.85, O=-0.84, and Na=+1. These are in close agreement with the model of Lehart (21). The isolated cage results will be extended to theoretical modelling of the intercluster interactions which contribute to the infrared absorption with increasing sodium atom loading, and which define the fully loaded cage and cluster band structure.

Framework Atom Substitution and Inter/Intracuster Geometry

An obvious way to tune the cluster electro-optic properties within a given structure is to change the cage and channel framework atomic composition. The net empirical charge is kept constant by isovalent substitution as exemplified in an isostructural molecular sieve series containing Al/Si, Ga/Si, Al/Ge, and Ga/Ge framework atoms.(24) This substitution does several things. It changes the average framework electronegativity, framework potential, band structure of the framework and consequently intercage coupling. It also modifies the inherent framework polarizability along with the linear and nonlinear optical properties. This has been supported by our recent studies of the nonlinear optical response of the four noncentrosymmetric sodalites with the above compositions (25). Second harmonic generation (SHG) measurements performed on the crystalline powders using Nd-Yag 1064 nm radiation showed that substitution of silicon by germanium in $\text{Na}_3\text{[(AlSiO}_4)_3 \cdot 4\text{H}_2\text{O]}$ and $\text{Na}_3\text{[(GaSiO}_4)_3 \cdot 4\text{H}_2\text{O]}$ increases SHG efficiency by factor of 3 while substitution of aluminum by gallium in $\text{Na}_3\text{[(AlSiO}_4)_3 \cdot 4\text{H}_2\text{O]}$ and $\text{Na}_3\text{[(AlGeO}_4)_3 \cdot 4\text{H}_2\text{O]}$ increases SHG by only 30%. Evaluation of the P43m point group $\chi_{(123)}$ nonzero polarizability tensor elements using the SHG measurements for this series is in progress.

The geometry changes associated with isovalent framework substitution also can dramatically affect both cluster geometry and diffusion properties through the pores. Structural parameters are given in Figure 7 for (1) a series of "empty" cage sodalite analogue structures filled with water, (2) an example of a dehydrated empty cage and (3) an anhydrous sodalite with a hydroxyl group at the center of the cage. Various framework compositions are indicated (26),(27),(28),(29). Several key points arise from these data.

Framework atomic radii in $\text{Na}_3\text{[(ZnAsO}_4)_3 \cdot 4\text{H}_2\text{O}]$ (27), (30) are 0.60Å (Zn²⁺) and 0.34Å (As⁵⁺) (cf 0.47Å (Ga³⁺) and 0.39Å (Ge⁴⁺)) so that one might expect to obtain for a given zeolite structural analogue the largest known pores and channels with the zinc arsenates. However, increasing the atomic radii of the framework metal atoms does not necessarily give either a larger cage or pore opening. This is indirectly evident from the lattice parameters for the cubic unit cells of the sodalite

analogue systems, and specifically is reflected in the decrease in the T-O-T' angles as the atomic radii increase (Figure 7).⁽³¹⁾ A is the area of the triangle of oxygen atoms which define the six ring pore openings of the sodalite cage. A and the pore openings *decrease* in size with increasing atomic radii.

δ is the distance of the sodium atom from the plane of the six ring tetrahedral atoms. If $\delta = 0$, the sodium atoms no longer have a single cage identity, and are equally shared between adjacent cages. At that point, as far as the sodium atoms are concerned, the structure is an expanded lattice with no definable sodium atom clusters. Upon dehydration of $\text{Na}_3\text{[(AlSiO}_4)_3 \cdot 4\text{H}_2\text{O]}$ there is a dramatic framework displacement of the 60 atom cage. The area of the pore opening increases 80% so that the structure becomes much more permeable. The T-O-T' angle increases 20° in going from $\text{Na}_3\text{[(AlSiO}_4)_3 \cdot 4\text{H}_2\text{O]}$ to $\text{Na}_3\text{[(AlSiO}_4)_3]$ and the sodium atom moves to within 0.24 Å of the center of the pore opening. 0.24 Å is the displacement required for the Na_3^{3+} cluster identity to be lost and the structure to be transformed into an expanded Na^+ lattice. The sodium atoms can be pulled back into a given cage by placing within the cage a charged species such as the hydroxyl ion. The consequence of this is a smaller T-O-T' angle and pore opening.

An example of the precision with which one can determine cluster and packaging structural properties in the sodalite systems is provided by our recent synthesis and characterization of the Ga/Ge sodalite structural analogue, $\text{Na}_3\text{[(GaGeO}_4)_3 \cdot 4\text{H}_2\text{O]}$. The site ordering of the framework atoms has a profound effect on the potential distribution, cluster geometry and electronic properties. From an X-ray diffraction point of view, one is asking to differentiate between two atoms which differ by one electron (Ga(31) and Ge(32)). MASNMR spectroscopy could partially resolve this question, but would not provide the structural details needed for the definition of optical-structural relationships. If indexed by "black box" software routines currently used, X-ray data for both polycrystalline and single crystal samples of $\text{Na}_3\text{[(GaGeO}_4)_3 \cdot 4\text{H}_2\text{O]}$ give a body centered lattice, space group I43m. Single crystal structure refinement in this space group (isotropic, no hydrogen atoms) converges to $R = 0.016$ and $R_w = 0.019$ with an average T-O distance of 1.791(1)Å for a disordered array of gallium and germanium atoms. A more careful examination of the single crystal diffraction data shows several reflections which are an exception to the body centered assignment with intensities $< 2\sigma(\text{background})$. Including these additional reflections in the space group P43n gives a refinement with $R = 0.012$ and $R_w = 0.014$ (isotropic, no hydrogen atoms). More important than this decrease in R factors, are the changes in the Ga-O (1.840(1)Å) and Ge-O (1.745(1)Å) bond distances, consistent with an ordered gallium/germanium framework. These results have been recently supported by ^{71}Ga MASNMR.

Other ways of varying the framework geometry are shown in Figure 8, for example, placing a relatively large atomic group such as MnO_4 -⁽³²⁾ at the center of the cage increases the pore size opening and moves the sodium atoms towards the center of the six ring opening. The metal atoms at the six ring sites are also closer to the expanded lattice

positions in the sodalite analog structures which have small cages because of small atomic radii (0.11 Å (B^{3+}), 0.27 Å (Be^{2+}) and 0.17 Å (P^{5+})).

In this connection, it is of interest to note that a comparison of the optical spectrum of Ag_4Br in $\text{Ag}_4[\text{Br}](\text{AlSiO}_4)_3$ (33), (34), (35) and $\text{Ag}_4[\text{Br}](\text{BePO}_4)_3$ (36) reveals a distinct red shift (~70 nm) in the optical spectrum in the latter. This is consistent with the cages being closer together (cage center - cage center 7.328(1) Å versus 7.17(1) Å); and, as noted above, with the silver atoms in the smaller BePO cages being closer to the center of the six rings and therefore to the expanded lattice configuration. These considerations may be secondary to changes in the framework electric field which are obtained by substituting Be for Al and P for Si. This is an example of the substitution shown in Table 2, giving in this case larger local gradients in the cage electric field. Additional experiments and theoretical modelling are currently underway in order to resolve the relative importance of the above possibilities.

A variety of five atom cluster combinations can be made with II-V, II-VI and III-V atoms packaged in the sodalite structure (Table 3). (37) The tetrahedral geometry of the first coordination sphere around the group VI atom in these structures is the same as that in the corresponding bulk semiconductor. The geometry of this coordination sphere can be substantially modified by the framework packaging. For example, the Zn-S distance for the five atom Zn_4S cluster is significantly shorter in the highly constrained borolite cage in $\text{Zn}_4\text{S}(\text{B}_2\text{O}_4)_3$ than in the larger beryllosilicate ($\text{Zn}_4\text{S}(\text{BeSiO}_4)_3$) or beryllogermanate $\text{Zn}_4\text{S}(\text{BeGeO}_4)_3$ cages (Table 3). In the latter two larger cage structures, the Zn-S distance approaches that observed in the bulk semiconductor. Framework substitution chemistry also changes the intercage distance and the "expanded lattice" nature of the cage by virtue of the siting of the zinc atoms. The systematic correlation of these structural changes with optical properties is of considerable interest and currently being investigated.

In summary, although the sodalite cages are relatively small and limit the size of the clusters which can be examined, they provide an excellent opportunity to investigate and model 3-d packaging of clusters. One can grow single crystals as large as a centimeter of several of these compositions. Because there is a large structure field with lattice parameters varying by as much as 20%, lattice matching to generate thin films is feasible. In addition, the six ring pores are sufficiently large so that gas and ion phase inclusion chemistry can be used to modify the framework and synthesize clusters. As noted above, these are noncentrosymmetric crystal structures with second order NLO properties. In the most common space group ($\text{P}43\text{n}$) for this structural field there is only one susceptibility tensor element, χ_{123} , which can be determined directly from powder data and used to evaluate structure/property relationships. The high optical density has already been demonstrated to give exceptional sensitivity and resolution in cathodo-chromic device applications based on F-centers in halogen and Ge-doped $\text{Na}_4\text{Br}(\text{AlSiO}_4)_3$ (38). Structurally it is possible to determine atomic positions and site occupancies precisely. The large accessible

compositional structural field also makes it possible to vary the framework band structure and charge over a wide range.

Other 3-D Packaging Considerations

The above approach for sodalite structure analogues is currently being extended to other periodic 3-d open framework hosts. Some specific goals (in addition to those noted previously) include:

- Stereoselective and orientational defined self assembly
- Larger channels and cage dimensions ($> 10\text{\AA}$)
- Definition of order/disorder properties
- Homogeneity and diffusion control

All of these have been sufficiently well demonstrated to confirm the feasibility of ultimately generating nanocomposite devices based on packaging in 3-d periodic hosts. Taking advantage of an organic guest/inorganic host approach, we have used polar molecular sieve channels to self assemble, orient and stabilize molecular arrays of hyperpolarizable organic molecules. Molecular self assembly has been monitored both on the external surface of zeolites by atomic force microscopy (AFM) (39) and within the pores by second harmonic generation. Orthogonal self assembly within the 3-d pores has been demonstrated by co-inclusion of two types of organic guests which have diametrically opposed non-linear optic responses (40), (41), (42). For example, para nitroaniline (NA) has a zero SHG response in the bulk since it is centrosymmetric, but can be oriented by the host channel polar axes of ALPO-5 to give a large SHG response. Conversely, 2 methyl para nitroaniline (MNA) has a large bulk SHG as a noncentrosymmetric phase, but because of the change in stereochemistry upon methyl substitution is not properly oriented in the channels of ALPO-5, giving a zero SHG response at all channel loadings. However NA can be used to co-assemble molecules of MNA and orient them in such a way as to generate as large an SHG response as for NA alone. Yet the two molecules have diametrically opposite (orthogonal) electro-optic properties in both the bulk and the polar channels of ALPO-5.

The primary limitation of the sodalite structures is the relatively small cage and pore size. The clusters per se have dimensions well below the exciton radius for the corresponding bulk semiconductors. The 120 atom 26-hedron cages of zeolites RHO and Y increase the possible cluster diameter to $\sim 11\text{-}13\text{\AA}$. The development of new larger pore molecular sieves is being actively pursued by numerous groups using Hoffman and 3-d linked molecular rod complexes (43), (44) for the building blocks of open framework structures, new approaches to molecular sieve synthesis and open frameworks containing both four and six coordinate metal ions. We will close with some recent results related to the last two items.

By carrying out molecular sieve synthesis at lower temperatures one can hope to accomplish several goals: 1) obtain more open structural

phases, 2) use the solvent as an effective structural template and 3) intercept metastable phases which have a short half-life at higher temperatures. The precedent for solvent templating is indicated by the work of Jeffrey in the late 1960's(45) who demonstrated that one could isolate and structurally characterize gas and ion-pair hydrates at low temperatures. An example is tetra(i-pentyl)ammonium fluoride which crystallizes at 31.2°C with an empirical formula $(\text{isoC}_5\text{H}_{11})_4\text{NF} \cdot 38\text{H}_2\text{O}$. In addition to the utility of tetra-alkyl ammonium fluorides as co-solvent mineralizers in zeolite synthesis(46),(47), their templating ability should be increasingly effective with decreasing temperature.

Using beryllium or zinc as framework metal atoms, we have isolated a number of open framework structures at room temperature or lower(27),(30),(48),(49) well within the regime of solvent clathrate templating. The molecular sieve chemistry of these new framework compositions is extensive. Using only the sodium ion as a template over a pH range from 1 to 13 gives nine different phases within a narrow temperature range of which five are open framework and one contains $(\text{ZnO})_2\text{PO}$ 3-ring configurations. Zeolite X can be synthesized at -18°C overnight using mixed templates (e.g. sodium and tetramethyl ammonium halide) and nonaqueous cosolvents. Organic template phases are equally prolific. 1,4-Diazabicyclo[2.2.2]octane (DABCO) gives seven distinct crystalline phases of which five are open framework structures. The zinc open framework structural field is expanded further when one considers the organophosphonates and phosphites which have been described by Clearfield(50),(51) and Mallouk.(52)

Nature has provided numerous intriguing examples of open framework structures containing both four and six coordinate metal atoms. Using a non aqueous solvent approach with organometallic precursors, we were able to synthesize hureaulite and alluaudite, two open framework iron phosphates.(53) More recently Haushalter has described a large number of reduced Mo(IV)-Mo(V) open framework phosphates.(54) Two other interesting members of the iron phosphate and arsenate mineral family are the 30 ring channel (free pore diameter 14.2Å) cacozenite $[\text{Al}(\text{Al},\text{Fe})_3\text{Fe}_{21}\text{O}_6(\text{OH})_{12}(\text{PO}_4)_{17}(\text{H}_2\text{O})_{24}] \cdot 51\text{H}_2\text{O}$ (55) and the smaller eight ring channel pharmacosiderite, $(\text{KFe}_4(\text{OH})_4(\text{AsO}_4)_3 \cdot 8\text{H}_2\text{O})$.(56) The latter is another example of a cluster of cages, the cages in this case being the M_4X_4 cubane structure (57), and has been synthesized as $\text{M}_4\text{Ge}_7\text{O}_{16}$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{H}$); $\text{M}_4(\text{TiO})_4(\text{SiO}_4)_3$ ($\text{M} = \text{K}, \text{Na}, \text{H}$); $\text{M}_4(\text{TiO})_4(\text{GeO}_4)_3$ ($\text{M} = \text{K}, \text{H}$) and $(\text{K},\text{H})_5(\text{FeO})_4(\text{AsO}_4)_3$.(58) In all cases there are 7-8 water molecules associated with the empirical formula. The germanium isostructure is shown in Figure 9.

Summary

3-d packaging with crystalline periodicity gives well defined structures with the flexibility to fine tune optical and electronic properties. This, along with recent advances in 3-d surface synthesis offer the opportunity to construct wires and cluster morphologies not readily accessible via 1-d layer confinement (1-d refers to the dimensionality of the

confinement) approaches. The continuing evolution of new 3-d periodic nanocomposite arrays and porous hosts generated in this research should also provide new materials for sorption catalysis and other areas of commercial and academic interest.

Acknowledgments

The authors thank the National Science Foundation (QUEST, Quantized Electron Structure Science and Technology Center, NSF-DMR 88-21499) Grants and the Office of Naval Research for support of this research.

Literature Cited

1. Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* (London) 1985, 318, 162-163.
2. Herron, N.; Wang, Y.; Eddy, M. M.; Stucky, G. D.; Cox, D. E.; Moller, K.; Bein, T. *J. Am. Chem. Soc.* 1989, 111(2), 530-540.
3. Barrer, R. M.; Cole, J. F. *J. Chem. Soc. A* 1970, 9, 1516-1523.
4. Fursenko, D. A. In *Fiz.-Khim. Issled. Mineraloobraz. Sist.*; Godovikov, A. A., Ed.; Akad. Nauk SSSR, Sib. Otd.; Inst. Geol. Geofiz.: Novosibirsk, USSR, 1982, pp. 104-107.
5. Barrer, R. M. In *Hydrothermal Chemistry of Zeolites*, Academic Press: London UK, 1982.
6. Hassan, I.; Buseck, P. R. *Am. Mineral.* 1989, 74, 394-410.
7. (Gier, T. E.; Harrison, W. T. A.; Stucky, G. D. *J. Chem. Mat.*, submitted for publication.)
8. Barrie, J. B.; Klinowski, J. *J. Phys. Chem.* 1989, 93, 5972-5974.
9. Barrer, R. M.; Cole, J. F. *J. Phys. Chem. Solids* 1968, 29, 1755-1758.
10. Smeulders, J. B. A. F.; Hefni, M. A.; Klaassen, A. A. K.; DeBoer, E.; Westphal, U.; Geismar, G. *Zeolites* 1987, 7, 347-352.
11. Geismar, G.; Westphal, U. *Chem.-Ztg.* 1987, 111, 277-280.
12. Breuer, R. E. H.; DeBoer, E.; Geismar, G. *Zeolites* 1989, 9, 336-340.
13. (Srdanov, V. I.; Haug, K.; Metiu, H.; Stucky, G. D. *J. Chem. Phys.*, submitted for publication.)
14. (Srdanov, V. I.; Margolese, D.; Saab, A.; Stucky, G. D. *Rev. Sci. Instr.*, submitted for publication.)
15. (Haug, K. and Metiu, H. *J. Phys. Chem.*, submitted for publication.)
16. Masuda, T.; Tsutsumi, K.; Takahashi, H. *J. Colloid Interface Sci.* 1980, 77, 238-242.
17. Barrachin, B.; CohendeLara, E. *J. Chem. Soc., Faraday Trans. 2* 1986, 82, 1953-1966.
18. Ito, T.; Fraissard, J. *J. Chem. Soc., Faraday Trans. 1* 1987, 83, 451-462.
19. Beran, S. *J. Mol. Catal.* 1988, 45, 225-233.
20. Van Genechten, G.; Mortier, W.J.; Geerlings, P. *J. Chem. Phys.* 1987, 86, 5063.
21. Leherste, L. *Chem. Phys. Lett.* 1988, 145, 237.
22. Vigne-Meader, F.; Auroux, A. *J. Phys. Chem.* 1990, 94, 316.
23. R. Skorczyk, *Acta Cryst.*, 1976, A32, 447.

24. (Harrison, W. T. A.; Gier, T. E. and Stucky, G. D. *J. Chem. Materials*, submitted for publication.)
25. (Harrison, W. T. A.; Gier, T. E. and Stucky, G. D. *J. Chem. Materials*, submitted for publication.)
26. Felsche, J.; Luger, S.; Baerlocher, C. *Zeolites* 1986, 6, 367-372.
27. Nenoff, T. M.; Harrison, W. T. A.; Gier, T. E.; Stucky, G. D. *J. Am. Chem. Soc.* 1991, 113, 378-379.
28. Keder, N.; Harrison, W. T. A.; Gier, T. E.; Zaremba, C.; Stucky, G. D. submitted for publication.)
29. Luger, S.; Felsche, J.; Fischer, P. *Acta Cryst.* 1987, C43, 1-3.
30. Gier, T.E. and Stucky, G.D. *Nature*, 1991, 349, 508-509.
31. A similar result has been observed by Newsam and Vaughan for the gallosilicate sodalite; Newsam, J. M.; Jorgensen, J. D. *Zeolites* 1987, 7, 569-573.
32. (Srdanov, V.; Harrison, W.T.A.; Cox, D. and Stucky, G.D., submitted for publication, *Inorg. Chem.*).
33. Stein, A.; Macdonald, P. M.; Ozin, G. A.; Stucky, G. D. *J. Phys. Chem.* 1990, 94, 6943-6948.
34. Stein, A.; Ozin, G. A.; Stucky, G. D. *J. Am. Chem. Soc.* 1990, 112, 904-905.
35. Ozin, G. A.; Kirkby, S.; Meszaros, M.; Ozkar, S.; Stein, A.; and Stucky, G. D. in *Materials For Nonlinear Optics: Chemical Perspectives*, American Chemical Society Symposium Series, Marder, S. R., Sohn, J. E. and Stucky, G.D. 1991, 455, 554-581.
36. (Gier, T. E.; Harrison, W. T. A. and Stucky, G. D. *Angewandte Chemie*, in press).
37. Moran, K. L.; Harrison, W. T. A.; Gier, T. E.; MacDougall, J. E.; Stucky, G. D. *Mater. Res. Soc. Symp. Proc.*, 1990, 164 (*Mater. Issues Microcryst., Semicond.*), 123-128.
38. Tranjan, F. M.; Todd, L. T. *J. Electrochem. Soc.* 1988, 135, 2288-2291.
39. Weisenhorn, A. L.; MacDougall, J. E.; Gould, S. A. C.; Cox, S. D.; Wise, W. S.; Massie, J.; Maivald, P.; Elings, V. B.; Stucky, G. D.; Hansma, P. K. *Science* 1990, 247, 1330-1333.
40. Cox, S. D.; Gier, T. E.; Stucky, G. D.; Bierlein, J. *J. Am. Chem. Soc.* 1988, 110, 2986-2987.
41. Cox, S. D.; Gier, T. E.; Stucky, G. D.; Bierlein, J. *Solid State Ionics*, 1988, 32-33, 514-520.
42. Cox, S. D.; Gier, T. E.; Stucky, G. D. *Chem. Mater.* 1990, 2, 609-619.
43. Iwamoto, T. *Inclusion Compounds, Volume 1*, Atwood, J. L.; Davies, J. D. D.; and MacNicol, D. D. Editors, Academic Press, New York, 1984, 29-57.
44. Robson, R., "Symposium on Supramolecular Architecture in Two and Three Dimension", American Chemical Society 201st National Meeting, Atlanta, GA (1991).
45. Jeffrey, G. A. In *Inclusion Compounds*; Atwood, J. L.; Davies, J. D. D.; MacNicol, D. D., Eds., Academic Press: New York, 1984, Vol. 1, pp. 135-190.
46. Suganuma, F.; Yoshinari, T.; Sera, T. *Jpn. Kokai Tokyo Koho* 1987, 6.

47. Xu, Y.; Maddox, P. J.; Couves, J. W. *J. Chem. Soc., Faraday Trans.* 1990, 86, 425-429.
48. Harrison, W. T. A.; Gier, T. E and Stucky, G. D. *J. Mater. Chem.* 1991, 1, 153.
49. Harrison, W. T. A.; Gier, T. E.; Moran, K. L.; Nicol, J. M.; Eckert, H.; Stucky, G. D. *Chem. Mater.* 1991, 3, 27-29.
50. Ortiz-Avila, C. Y.; Squattrito, P. J.; Shieh, M.; Clearfield, A. *Inorg. Chem.* 1989, 28, 2608-2615.
51. Ortiz-Avila, Y.; Rudolf, P. R.; Clearfield, A. *Inorg. Chem.* 1989, 28, 2137-2141.
52. Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Inorg. Chem.* 1988, 27, 2781-2785.
53. Corbin, D. R.; Whitney, J. F.; Fultz, W. C.; Stucky, G. D.; Eddy, M. M.; Cheetham, A. K. *Inorg. Chem.* 1986, 25, 2279-2280.
54. Mundi, L.A., Strohmaier, K.G.; Haushalter, R.C. *Inorg. Chem.* 1991, 30, 153 and included references.
55. Moore, P. B.; Shen, J. *Nature* 1983, 306, 356-358.
56. Buerger, M. J.; Dollase, W. A.; Garaycochea-Wittke, I. Z. *Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* 1967, 125, 92-108.
57. Hauser, E.; Bittner, H.; Nowotny, H. *Monatsh. Chem.* 1970, 101, 1864-1873. Nevskii, N. N.; Plyukhin, V. V.; Ivanova, L. I.; Belov, N. V. *Dokl. Akad. Nauk SSSR* 1979, 245, 110-111, [Crystallogr.].
58. (Harrison, W. T. A.; Gier, T. E.; Stucky, G. D. *Chem. Comm.*, submitted for publication).

Table Captions

- Table 1. Examples of the number of atoms that can be put in a single sodalite cage.
- Table 2. Formal charge variation with framework composition. The corresponding total formal charge variation within the sodalite cage is from 0 to -6.

Figure Captions

- Figure 1. 60 Atom truncated octahedron of the sodalite structure with oxygen atoms included (bottom) and excluded (upper right) compared with C_{60} truncated icosahedron.
- Figure 2. M_4X_4 cubane-like cluster in sodalite structure cage.
- Figure 3. Five atom M_4X sodalite cage cluster along with MX fragments from surrounding cages.
- Figure 4. Absorption spectra (absolute scale) for Na_4^{3+} centers in sodium sodalite at Na_4^{3+}/Na_3^{3+} loadings of 1:2, 4, 10 and 50.
- Figure 5. Calculated absorption cross section of Na_4^{3+} cluster in a sodalite cage at high dilution with framework and sodium atom charges indicated, a) an interpolation between the charges of Si = 0.0, Al = 0.0, O = -0.25, and Na = 1.0 (22) and the charges given by Leherter (21); b) reference (21); c) reference (20); d) an interpolation between the charges of Van Genechten (20) and the much stronger charge model of Skorczyk (23) which places a charge of 3.03 on Si, 2.45 on Al, -1.62 on O.
- Figure 6. Theoretical orientationally averaged high resolution spectrum of a single Na_4^{3+} cluster in a sodalite cage at high dilution with atomic charges of Si=+1.5, Al=0.85, O=-0.84 and Na=+1 (top) and observed absorption spectrum $Na_4^{3+}:Na_3^{3+} = 1:50$.
- Figure 7. Sodalite framework composition modification of cage structure for hydrated empty cages.
- Figure 8. Use of cage packaging to control cluster and intercluster geometries.
- Figure 9. $K_4Ge_7O_{16}$ channel structure. (57,58)

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)*
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia 22217-5000

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Air Weapons Center
Weapons Division
China Lake, CA 93555-6001

Dr. Elek Lindner (1)
Naval Command, Control and Ocean
Surveillance Center
RDT&E Division
San Diego, CA. 92152-5000

Dr. Bernard E. Douda (1)
Crane Division
Naval Surface Warfare Center
Crane, Indiana 47522-5000

Dr. Richard W. Drisko (1)
Naval Civil Engineering
Laboratory
Code L52
Port Hueneme, CA 93043

Dr. Harold H. Singerman (1)
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. Eugene C. Fischer (1)
Code 2840
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Defense Technical Information
Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

* Number of copies to forward